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A Study of the Vogel Reaction for the Determination of Cobalt.

Charles Gosse De vries

Louisiana State University and Agricultural & Mechanical College

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**A STUDY OF THE VOGEL REACTION
FOR THE DETERMINATION OF COBALT**

A Dissertation

**Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy**

in

The Department of Chemistry

**by
Charles Gosse de Vries
A.B., West Virginia University, 1941
M.S., Louisiana State University, 1948
June, 1949**

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ABSTRACT

An explanation for the blue color formed in the Vogel reaction is proposed. Investigations show that pink aqueous solutions containing cobalt(II) and thiocyanate ions have the complexes $\text{Co}(\text{NCS})^{\dagger}$ and $\text{Co}(\text{NCS})_6^{\ddagger}$ present while the blue color formed when excess alcohol is added to the system is produced when the complex $\text{Co}(\text{NCS})_6^{\ddagger}$ is present. The number of water molecules in the coordination sphere of the first complex is undetermined. That the blue color is associated with configurations within the cobalt atom itself is indicated by the fact that addenda other than thiocyanate may give complexes showing the same spectral characteristics as the thiocyanate compound. Likewise, various alcohols used to develop the color in this reaction all produce colors having similar characteristics.

INTRODUCTION

Cobalt(II) salts react with thiocyanate ions to form complexes which are soluble in water and which have colors of approximately the same hue as hydrated cobalt(II) ions. Upon addition of organic solvents, such as ethyl alcohol or acetone, a blue color is produced; this color formation is important for the detection and determination of cobalt, and the present study was undertaken to establish the nature of this color and the mode of its formation.

REVIEW OF THE LITERATURE

Vogel (36) reported the following reaction as a specific test for the cobalt(II) ion. The test, which now bears his name, consists of treating an unknown solution with solid ammonium thiocyanate after which acetone is added. In the presence of cobalt(II) a blue color results.

There have been many modifications of this test. Moller (27) gave references dealing with the combination of ammonium thiocyanate solution with amyl alcohol and other mixtures as solvents. McAlpine and Seale (26) described this reaction as did Bettink (3).

Other suitable solvents found were: acetone, recommended by Feigl and Stern (14), Ditz (8) and Kolthoff (19); amyl alcohol (7), (10), (30) and ethyl alcohol (9), (29), (37).

Cyclic compounds which may serve to indicate the cobalt(II) ion in a thiocyanate salt solution are furfural (33), (34) and benzyl alcohol (6).

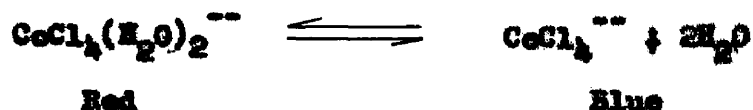
Ions other than thiocyanate have been investigated. The blue color is produced when thiosulfate ions are used (22) and the sensitivity of the reaction is said to be increased if ammonium cyanate is used instead of ammonium thiocyanate (12).

The cobalt-thiocyanate complex is not only useful in the detection of cobalt but also lends itself to the quantitative determination of this metal. One method reported by Rosenheim and Ehlshinsky (31) and Moller (28) was the use of standard solutions and comparison with the unknown. An ether-alcohol mixture was used for the development of color.

Mader (25) produced the color with amyl alcohol and with acetone. Photometric measurements permit the determination as little as 0.005% cobalt in solution.

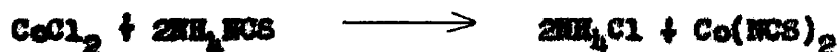
The amount of cobalt in ores may be found by using the cobalt-thiocyanate complex and an amyl alcohol-ether mixture (40). Either visual or photoelectric methods of measurement are suitable.

Although a number of theories have been postulated to account for the blue color, no definite explanation is available. Hill and Howell (16) proposed that the color change in cobalt(II) solutions is due to the dehydration of a cobalt(II)-hexaquo complex ion. In strongly acidic medium (concentrated mineral acids) the color of the solution is blue conforming to the reaction:

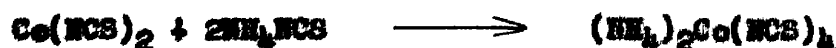


This dehydration theory was not accepted by Barsett and Croucher (1). They claimed that the reasoning of the former, which was based on the comparison of magnesium and cobalt oxide, was unjustified and hence cobalt need not be coordinated to six water molecules.

The addition of a concentrated solution of ammonium thiocyanate to a solution of a cobalt(II) salt could be represented by:



and



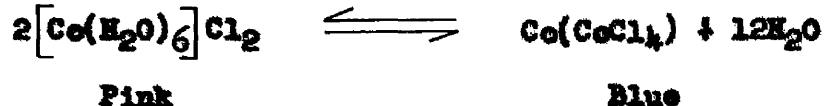
according to Mellor (27).

Reesi (32) bubbled dry hydrogen chloride through a 0.1 M aqueous $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ solution. The solution changed from a pink to a blue

color. He believed that the color is caused by a compound formation of the type:



One possible explanation as to the formation of the color by dehydration may be shown by the equation (11):



Feigl (13) explained that the blue color is probably due to solvate formation with complex cobalt-thiocyanates such as $\text{K}_2[\text{Co}(\text{NCS})_4]$. Upon dilution the color returns to pink. This appears as the result of the formation of the $\text{Co}(\text{NCS})_4^{--}$ ions (12).

Young and Hall (40) pointed out that the capacity of a solvent for preventing decomposition of a complex varies inversely as its dielectric constant and that the complex formed with cobalt and ammonium thiocyanate is extracted from aqueous solutions by organic solvents.

Absorptancy curves have been run on solutions of cobalt thiocyanate in non aqueous solvents. In a non aqueous solvent, L, the complex $\text{Co}(\text{NCS})_2\text{L}_2$ is formed (18). The complex $\text{Co}(\text{NCS})_4^{--}$ is present in aqueous solutions containing an excess of cobalt while an excess of thiocyanate produces $\text{Co}(\text{NCS})_4^{--}$ (17).

EXPERIMENTAL

By means of the Jander equation (21) ionic weights of some complexes can be determined polarographically. The diffusion current coefficient of the ion under investigation is found by obtaining a polarogram of that ion and then using the Ilkovic equation (20).

$$i_d = 605 C n D_m^{1/2} t^{1/6}$$

- i_d = diffusion current in micro amperes.
 n = number of faradays of electricity required per molar unit of the electrode reactant.
 D = diffusion current coefficient of the reducible or oxidizable substance.
 C = concentration in millimoles per liter.
 m = rate of flow of mercury in milligrams per second.
 t = drop time in seconds.

The Jander equation, which follows, is applied and the ionic weight determined.

$$M_x = \frac{Z_k D_k}{Z_x D_x} M_k$$

- M_x = ionic weight of the unknown ion.
 M_k = ionic weight of the known ion.
 Z_k = viscosity of the known solution.
 D_k = diffusion current coefficient of the known ion.
 D_x = diffusion current coefficient of the unknown ion.

The viscosity (Z) of the solution is calculated from

$$Z_x = Z_{H_2O} \frac{d_x t_x}{d_{H_2O} t_{H_2O}}$$

Z_{H_2O} = viscosity of water in poise.

Z_x = viscosity of unknown in poise.

d_x = density of solution in grams per milliliter.

t_x = time for the unknown to drain through Ostwald viscometer.

d_{H_2O} = density of water.

t_{H_2O} = time for an equal amount of water to drain through Ostwald viscometer.

A shift of the half-wave potential in a polarogram indicates complexation and the coordination number can be calculated from it (23). Thus, polarography seemed a logical approach to the present problem.

A suitable organic solvent as a developer of the blue color was chosen using the following criteria: one, it must not be oxidizable or reducible at the half-wave potential for the complex; two, it must not be so viscous that it interferes with polarographic measurements; three, it must have a different weight from the NCS^- ion. The purpose of the first criterion is obvious, while the second restriction is necessitated by the viscosity factor in the Jander equation. If the solvent were coordinating, a weight difference is needed to show it, hence the third restriction.

Of the organic solvents tested acetone gave the deepest color. Polarograms of the cobalt, thiocyanate, water and acetone system exhibited irregularly shaped curves indicating a half-wave potential for the reduction of the acetone near that of the cobalt complex. Thus acetone was unsuitable since it did not meet requirement number one.

Dichloroacetic acid, diethylcarbonol and formaldehyde were tested but even when added in considerable excess none gave a blue color. Both formic acid and n-butyl alcohol were rejected because the resulting test produced only a light blue color.

Isopropyl alcohol and n-propyl alcohol gave tests with the cobalt-thiocyanate-water system; however, requirement three was not met by these solvents.

Two solvents, diethylene glycol and tert-amyl alcohol were too viscous to be used for polarographic study.

The criteria of a good solvent to be used in these investigations were met by ethyl, methyl and tert-butyl alcohols. These three were used as developers in the polarographic studies.

Data were gathered for the determination of the ionic weight using a Sargent Model XI Polarograph. It was hoped that a formula for the complex causing the blue color could be deduced from measured ionic weight. Results are shown in Table I. The trioxalatocobaltate ion was used as the standard or "known" (5) in the ionic weight determinations. Even though viscosity effects were taken into consideration, larger diffusion currents were obtained than those anticipated. It is seen that by using different solvents the ionic weights given by Jander's equation are improbable. This difference in diffusion current (step height) might be credited to a difference in dielectric constant. There is little information regarding the effect of dielectric constant upon the diffusion current coefficient. It is known, however, that in solutions having smaller dielectric constants, the heights of the waves of the diffusion currents were smaller, as a rule, at the same concentration of the substance undergoing the reduction. When no interaction occurred between the ion and the solvent, a direct proportion

TABLE I

Ionic Weights Determined Polarographically

Solu- tion	Setting mA/mm	Step mm	Ht. mm	i_d mA	n	C	milli- moles	t sec	$t^{1/6}$	m	$m^{2/3}$	$D^{1/2}$ $\times 10^{-3}$	D $\times 10^{-6}$ sq cm per sec	t_x sec	d_x gms	Z_x poise	Molecular Weight
For first Ostwald viscometer used 82.3 0.997 0.894																	
H ₂ O																	-
1	0.392	73.4		28.8	1	9.87	4.65	1.29	1.97	1.57	2.39	5.69	107.0	1.12	1.06		323
2	0.392	67.0		26.3	1	9.40	5.10	1.31	1.98	1.58	2.24	4.98					323
5.23 (From Kolthoff & Waters (21) used in calculations)																	
3	1.10	50.0		54.9	2	9.92	4.65	1.29	1.97	1.57	2.26	5.10					408
4	1.10	45.0		49.4	2	9.92	4.65	1.29	1.97	1.57	2.03	4.13					419
5	1.10	41.5		45.5	2	9.92	4.65	1.29	1.97	1.57	1.87	3.51					408
For second viscometer used																	
H ₂ O																	-
6	1.097	37.5		40.8	2	9.92	4.65	1.29	1.97	1.57	1.69	2.81					450
7	1.097	33.0		36.2	2	9.92	4.65	1.29	1.97	1.57	1.49	2.22					525
8	0.392	81.0		31.8	2	9.79	4.74	1.30	1.98	1.58	1.31	1.72					547
9	0.392	49.1		19.2	2	9.79	4.74	1.30	1.98	1.58	0.790	0.623					1780
10	0.392	111.0		43.5	2	9.79	5.10	1.31	1.98	1.58	1.78	3.13					484
11	0.392	100.0		39.2	2	9.79	5.10	1.31	1.98	1.58	1.60	2.57					610

1 and 2 1 M in $K_2C_2O_4$, 0.2 M in $(NH_4)_2C_2O_4$, 0.5 M in HAC, 0.02% in gelatin, molarity in $K_3Co(C_2O_4)_3$, the ion, M_x , used in future calculations is indicated.

3 1 M in KSCN, 5% in tertiary butyl alcohol, 0.02% in gelatin, molarity of Co(II) as indicated

4 Same as 3 only 10% tertiary butyl alcohol

5 Same as 3 only 15% tertiary butyl alcohol

6 Same as 3 only 20% tertiary butyl alcohol:

7 Same as 6 only 25% tertiary butyl alcohol

8 Same as 6 only 30% tertiary butyl alcohol

9 Same as 6 only 50% tertiary butyl alcohol

10 Same as 6 only 30% methyl alcohol used

11 Same as 10 only 50% methyl alcohol used

Second viscometer used

At 25° C

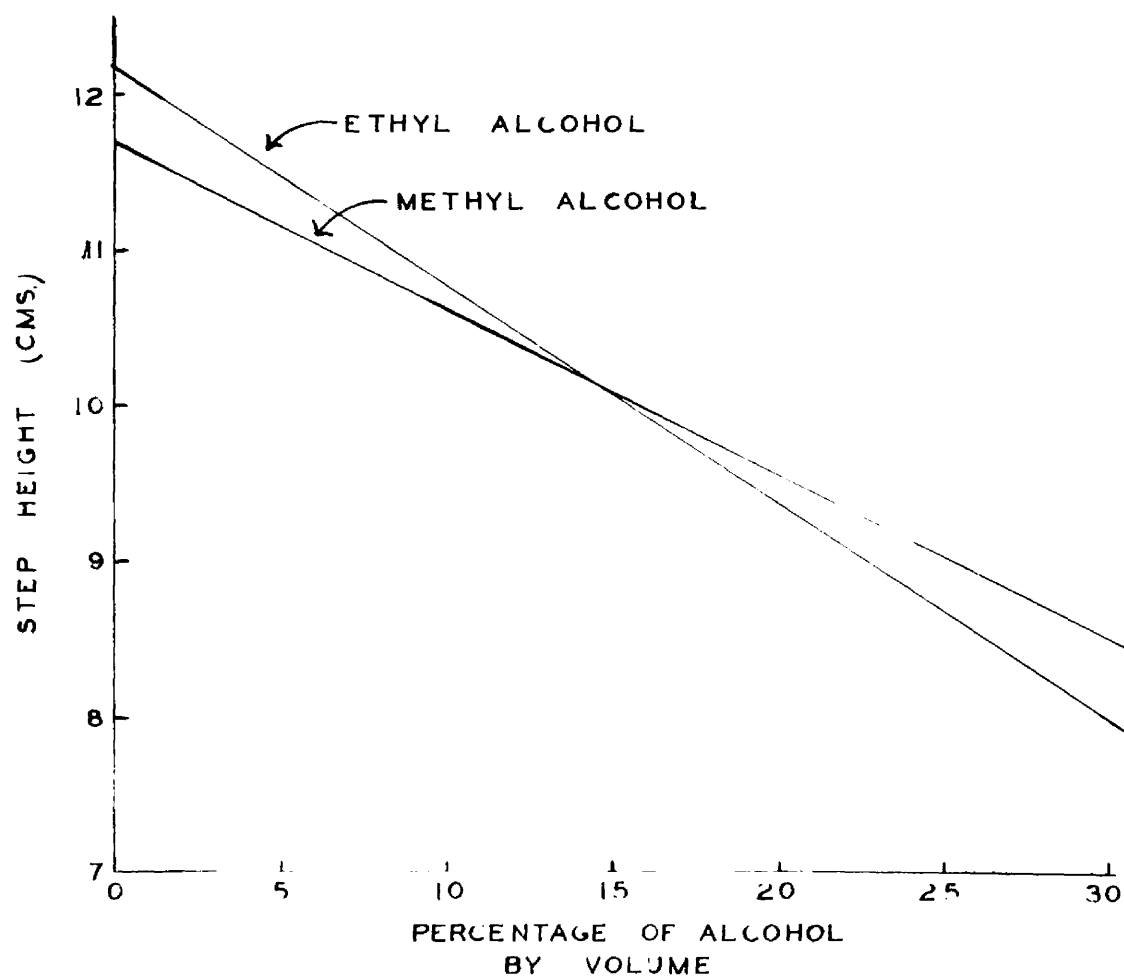
existed between the height of the wave and the concentration of the ion reduced (41). Abnormally large step heights have been reported in the use of systems containing a high percentage of sugar. The diffusion currents became systematically higher as the viscosity increased. An explanation for the anomalous diffusion currents in sugar solutions may lie in some action of the dielectric properties on the interionic attraction (35).

From these data it appeared that no definite ionic weight could be assigned to the complex giving the blue color because of the various uncontrollable factors pertaining to the polarographic method. To determine qualitatively if complexation occurred a series of studies were made on cobalt-thiocyanate solutions having varying amounts of organic solvent and ranging in color from pink to blue (Figure 1). Both ethyl and methyl alcohol were used. Since the step height of the polarogram is an indication of the ionic weight a curve of step height versus percentage by volume of organic solvent was plotted. Due to the changes in density and other factors the step height declined. No break in the curve occurred hence giving no indication of a new type ion formed at a definite water-alcohol mixture.

The salt, potassium selenocyanate, was prepared following the method outlined in "Inorganic Syntheses Vol. II" (15). It was found that a blue color is produced by mixtures of this salt, cobalt(II) ions and ethyl alcohol. The procedure used with KNCSe was the same as that used in the KNCS studies and similar results were obtained.

Next a series of tests were made with a solvent having a fixed ratio of alcohol to water, and the amount of potassium thiocyanate varied. In this way the dielectric constant remained fixed. Polarograms

FIGURE 1
EFFECT OF ALCOHOL
ON STEP HEIGHT



SOLUTION : 0.00979 M IN $\text{Co}(\text{II})$

0.02 % IN GELATIN

0.5 M IN KNO_3 AT 25°C .

obtained in these cases showed that the step height remained constant after a ratio of Co(II) to NCS^- of 1 to 4 was obtained. Between the ratio of 1 to 4 and 1 to 1 the step height gradually increased. However, using potassium chloride, which did not give the blue color, the same phenomena occurred (Table II). This has been observed before (33) and is attributed to the movement of the indifferent electrolyte at the surface of the cathode which depends upon the concentration of this electrolyte. Sodium thiosulfate which gave the blue color was also used in these studies. At the same ratios and concentrations the step heights with all three salts were practically the same.

When potassium chloride was used as a supporting electrolyte a break in the wave was noted. According to Lingane (24) it is caused by the reduction of the hydroxypentaaquo cobalt(II) ion and disappears upon acidification. No such wave occurred when NCS^- or $\text{S}_2\text{O}_3^{--}$ ions were used as supporting electrolytes. Because of this, these are recommended for use in polarographic determinations of cobalt.

The half-wave potential of the cobalt wave in thiosulfate solution was more positive than that obtained in thiocyanate solutions. The wave obtained in thiocyanate solutions in turn was more negative than that obtained in chloride solutions.

Since a change in density causes a change in step height as does change in ionic concentration both were held constant over a range of values for thiocyanate ion concentration. By having the same amount of alcohol in each sample the same macro dielectric constant was held throughout this phase of investigation. As the amount of potassium thiocyanate was reduced in the system the ionic concentration was held constant using an indifferent electrolyte, sodium acetate. The polarograph recorded no noticeable change in ionic weight (step height), while

TABLE II
Variation of Step Height with Change in
Supporting Electrolyte Concentration

Solution	Ratio of Supporting Electrolyte to Cobalt	Step Height mm.
1	50:1	30.0
2	40:1	30.0
3	30:1	30.0
4	20:1	30.0
5	10:1	30.0
6	8:1	30.0
7	6:1	30.0
8	4:1	32.0
9	2:1	35.0
10	1:1	38.0
11	50:1	34.0
12	1:1	41.0
13	50:1	34.0
14	1:1	41.0
15	50:1	34.0
16	1:1	40.0

Solutions 1-10 KNCs, 0.02% in gelatin, 30% in ethyl alcohol
0.098 M in cobalt.

11-12 Same as 1 to 10 only KCl

13-14 Same as 1 to 10

15-16 Same as 1 to 10 only $\text{Na}_2\text{S}_2\text{O}_3$

the color of the system changed from blue to pink (Table III). The half-wave potential ($E_{\frac{1}{2}}$) did shift which might be expected when changing from a supporting electrolyte of potassium thiocyanate to sodium acetate.

From the foregoing it is seen that the polarograph did not reveal any change in ionic weight going from the blue to pink color; also the restrictions of the system prevent using change of the half-wave potential to determine any change in coordination number if such occurred.

Spectrophotometry was next employed as a means of studying the nature of the blue color. Brode (4) has determined the structure of complexes by spectrochemical means. In this method a series of curves are obtained for the system under consideration. Each curve is different from the rest when there is a variation in the amount of one of the members of the system. The amount of complexation is indicated by changes in the curve.

In these investigations a Beckman Model DU Spectrophotometer was used. At the outset data were gathered for various systems and the curves drawn (Figure 2). The optical density, D , versus wave length in millimicrons, $m\mu$, was plotted. A simple system of cobalt(II) ions in water was obtained first and then the system changed by adding different electrolytes. A change in intensity in the red region, $510 m\mu$, was observed. Systems which contained different alcohols were investigated next. This change in the system caused an absorptance peak to occur in the blue region of the spectrum; the peak of absorptance in each of these cases was at $620 m\mu$. Feigl (13) noted that the absorptance curve is the same regardless of solvent used. These studies showed further that the peak in the blue region was at the same point, $620 m\mu$,

TABLE III

Step Heights with Cobalt Concentration, Ionic
Concentration and Alcohol Concentration Held Constant

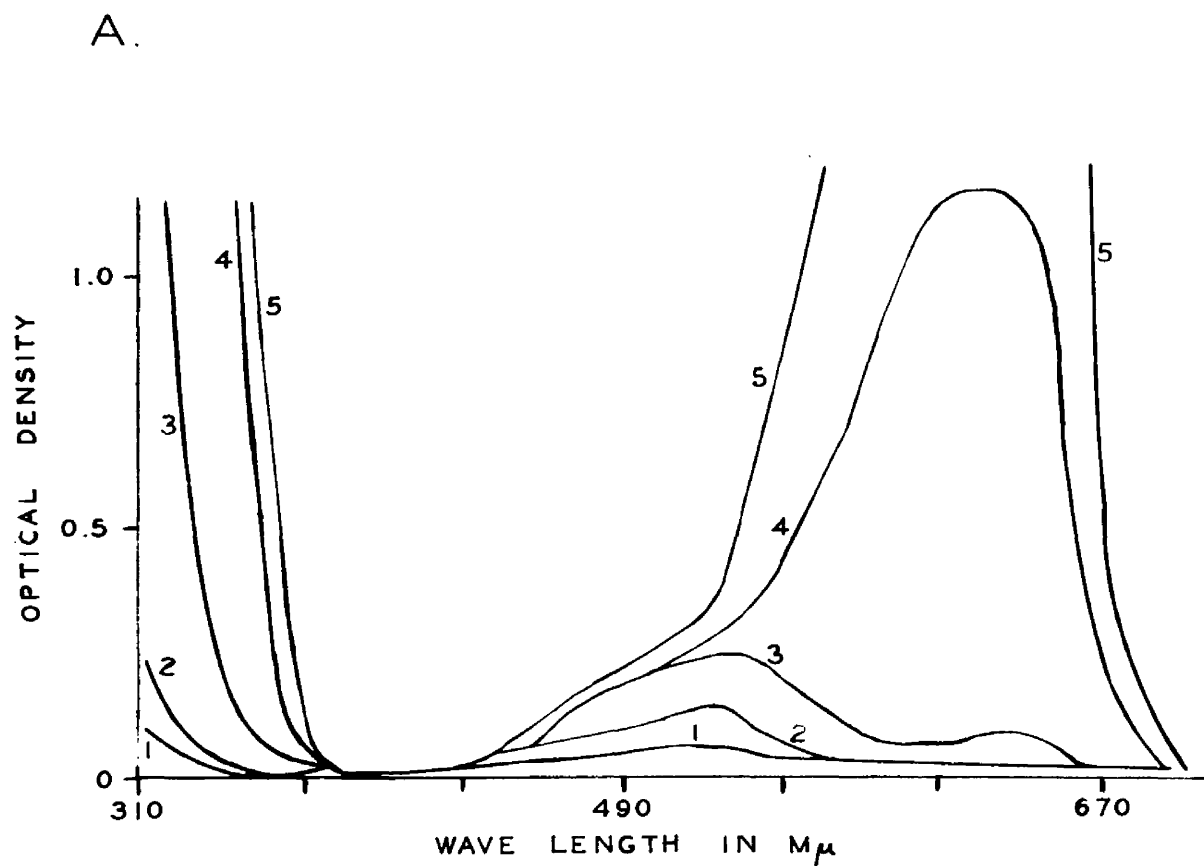
Solution	NaAc (molarity)	KNCS (molarity)	Step Height mm.	$E_{1/2}$
1	0.20	0	92	-0.948
2	0.05	0.15	91	-1.09
3	.025	0.175	90	-1.17
4	.010	0.19	89	-1.23
5	0	0.20	87	-1.56

$E_{1/2}$ against S.C.E.

30% ethyl alcohol - 0.02% gelatin

FIGURE 2

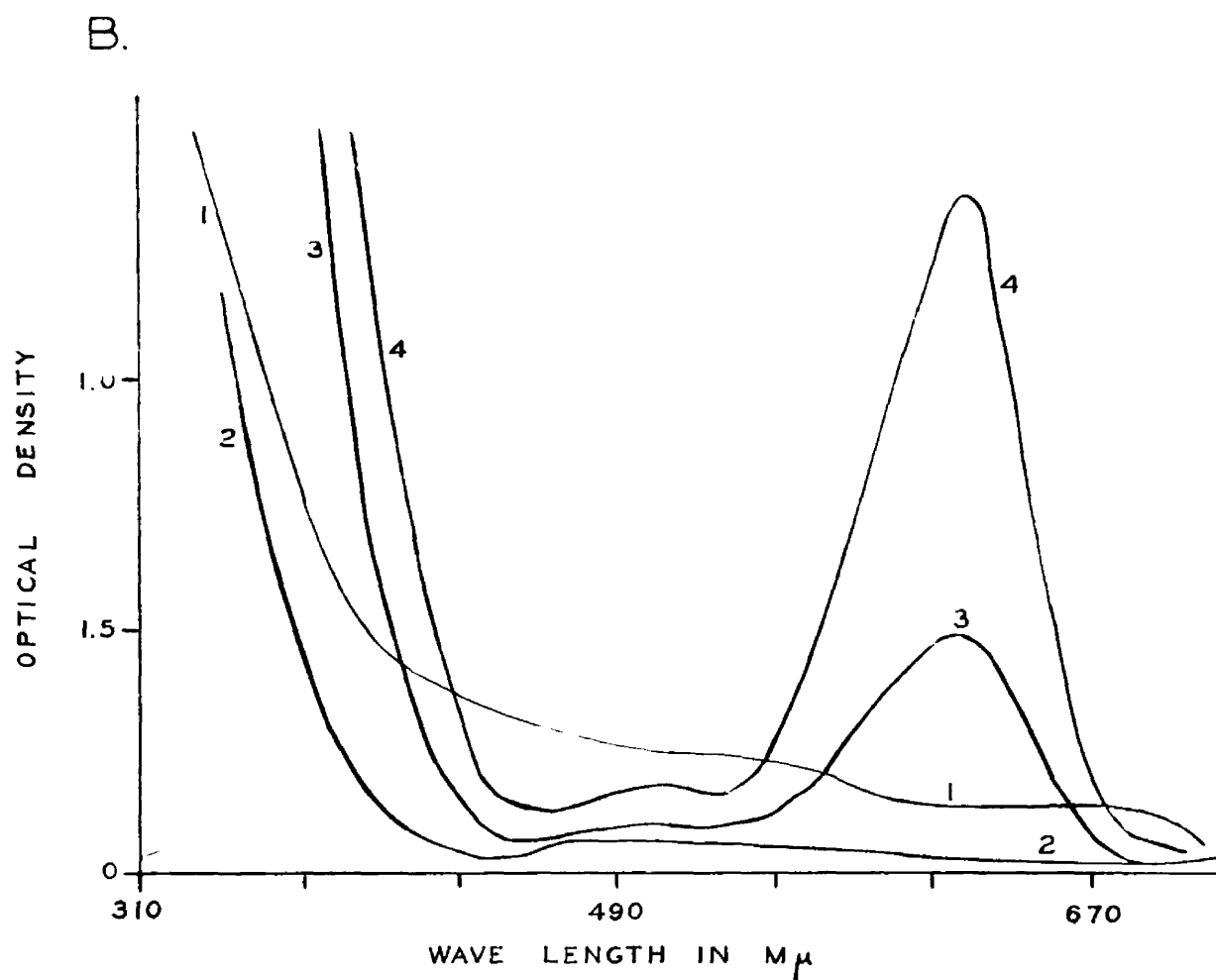
SPECTRAL ABSORPTANCY CURVES



A.

1. Co(II) , H_2O
2. Co(I) , H_2O , NCS^-
3. Co(II) , H_2O , NCS^- ,
METHYL ALCOHOL
4. Co(II) , H_2O , NCS^- ,
ETHYL ALCOHOL
5. Co(II) , H_2O , NCS^- ,
T-BUTYL ALCOHOL

FIGURE 2
SPECTRAL ABSORPTANCY CURVES



B.

1. Co(II) , H_2O , NCS e^-
2. Co(II) , H_2O , NCS e^- ,
METHYL ALCOHOL
3. Co(II) , H_2O , NCS e^- ,
ETHYL ALCOHOL
5. Co(II) , H_2O , NCS e^- ,
T-BUTYL ALCOHOL

(SOLUTIONS UNSTABLE)

in systems which had different ions to develop the blue color. Water solutions of the potassium selenocyanate salt were found to be stable for only a short period of time. Without further work it would prove undesirable as a reagent for the cobalt test.

A method of curve variation similar to that of Brode (5) and Kiss and Cakan (17) was used on water-alcohol systems with results shown in the series of curves, Figure 3. With the ratio of water to alcohol held constant the ratio of cobalt to thiocyanate was varied (Figure 3 A). The optical density curves shown in Figure 3 B, C, D, E and F are of solutions containing ratios of cobalt to thiocyanate of 1 to 5, 1 to 6 and 1 to 7. Solvent composition was varied from 0% ethyl alcohol to 50% ethyl alcohol. These data showed a deepening of color at a wave length of 620 mμ when either the thiocyanate to cobalt or alcohol to water ratio was increased. However, the structure of the ion responsible for the deepening of the color could not be deduced by this method.

According to Vosburgh and Cooper (38) the ratio of complexation can be determined by means of a spectrophotometer using Job's method of continuous variation. Equimolecular solutions of the ions were used and they varied the proportions of each from 100% to zero while the total molarity was kept constant. A plot was made of the difference in optical density at a given wave length versus the mole fraction of complexing ion. This difference was obtained by subtracting the optical density given by straight dilution of the system from that obtained from the addition of the non-colored complexer.

Vosburgh and Cooper developed the following expression to determine the amount of complexation:

FIGURE 3
CURVE VARIATION

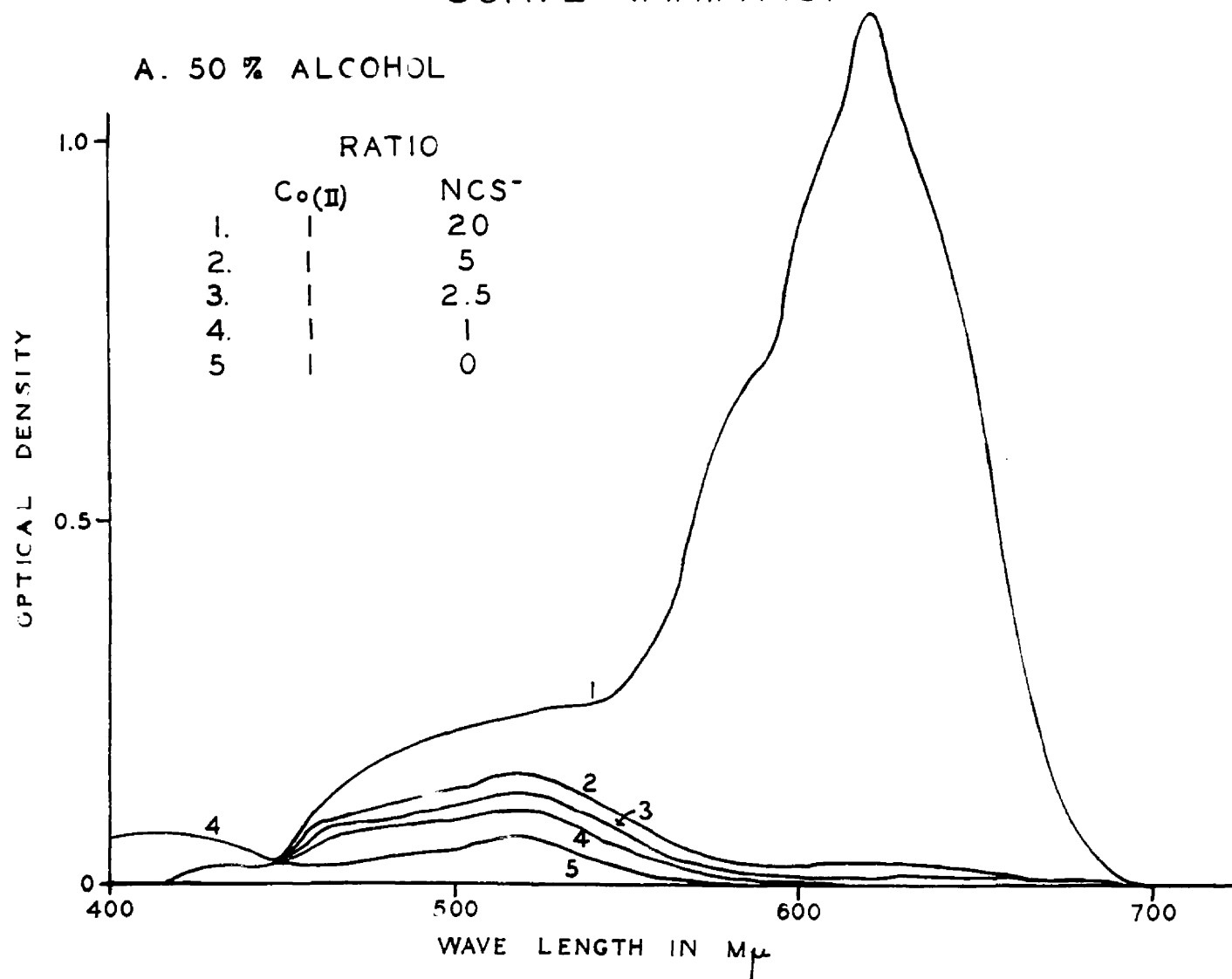
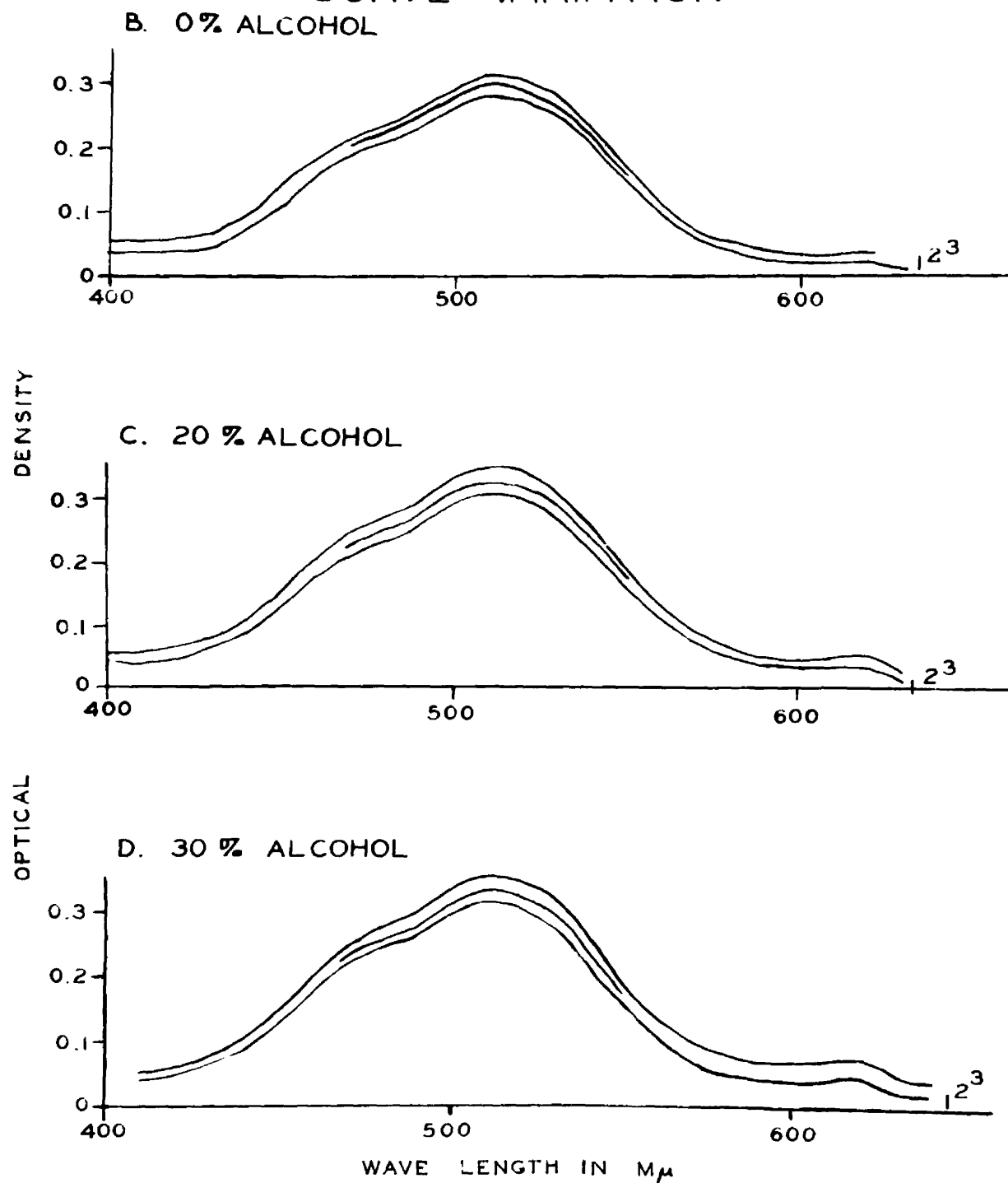


FIGURE 3

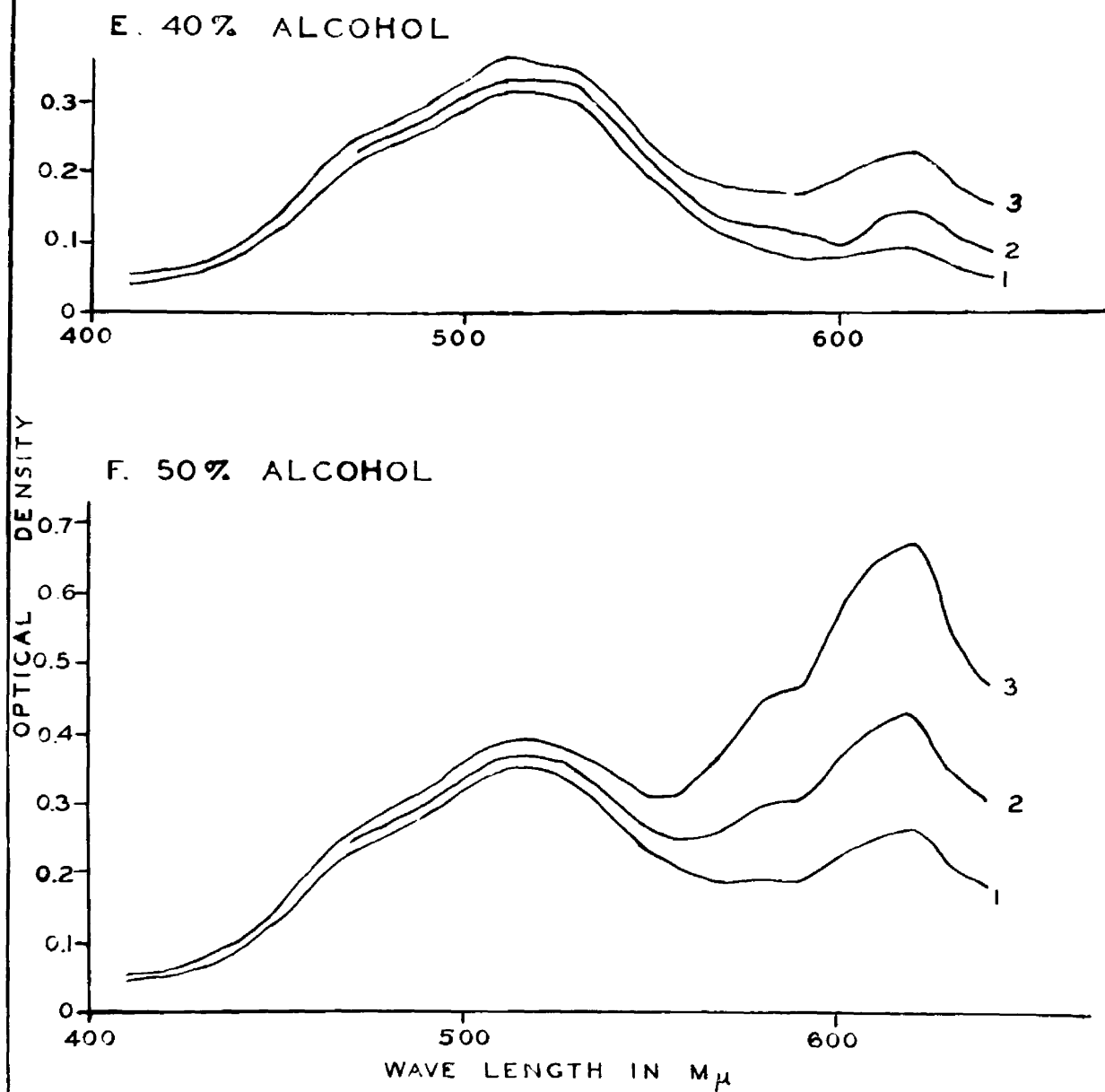
CURVE VARIATION



	RATIO	
	Co(II)	NCS ⁻
1.	1	5
2.	1	6
3.	1	7

0.177 M Co(II)

FIGURE 3
CURVE VARIATION



	RATIO	
	$Co(II)$	NCS^-
1.	1	5
2.	1	6
3.	1	7
0.177 M $Co(II)$		

$$N = \frac{x}{1 - x}$$

where

N = coordination number

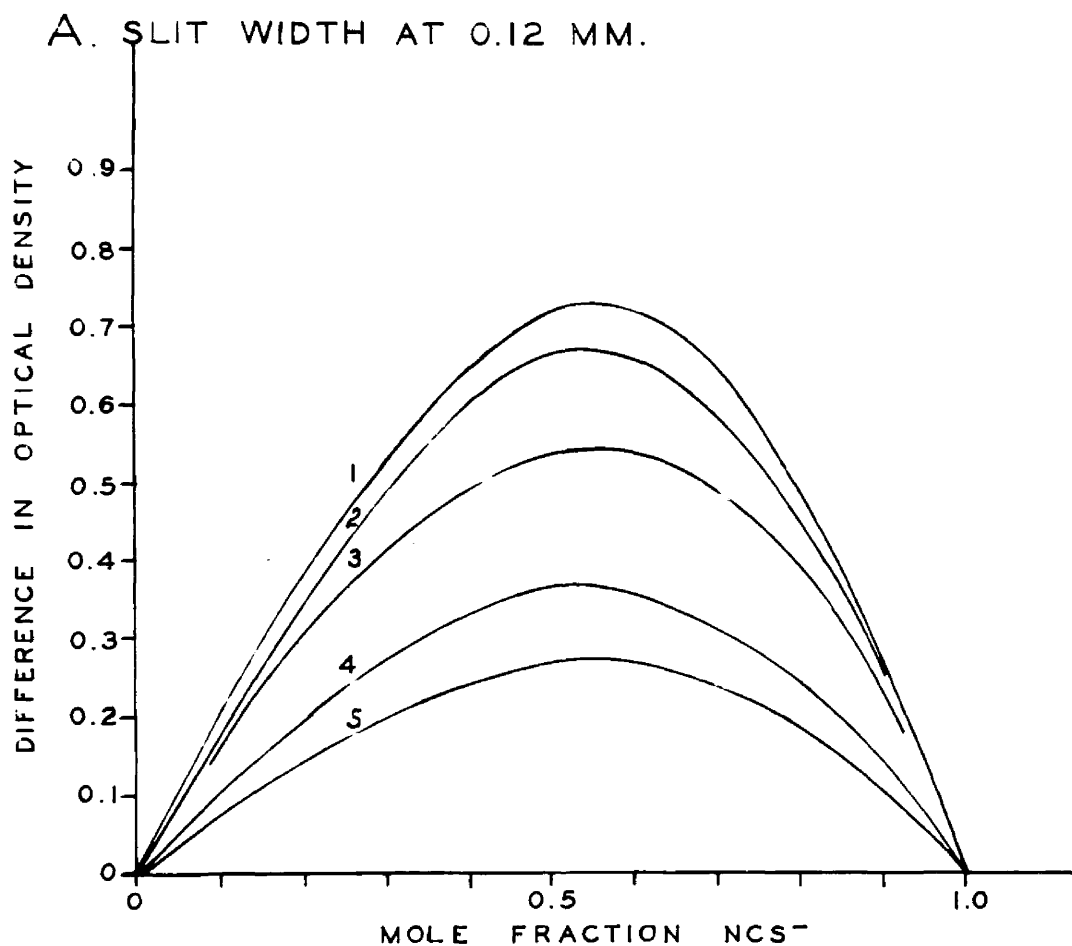
x = amount of complexing ion present at maximum difference in optical density.

Job's method was applied to the cobalt-thiocyanate system and the above formula used. For aqueous solutions N was found to equal one, indicating that a mixture of Co(II) and NCS^- ions may contain some Co(NCS)^+ ions in solution. This was found to hold for several wave lengths (Figure 4 A).

The effect of adding alcohol to the system was studied. Data were obtained using two Beckman Spectrophotometers. In one instance the slit width was in the range of 0.15 mm and in the other, the slit width in the range of 0.04 mm was used. As before, water solutions of cobalt-thiocyanate were examined both in the red and in the blue regions (Figure 4 A and B). Cobalt-thiocyanate solutions were prepared by adding the necessary amounts of cobalt nitrate and potassium thiocyanate solutions, 10 milliliters of absolute ethyl alcohol and enough distilled water to make a total volume of 25 milliliters. Again Job's method was used and data obtained in both spectral regions. Figure 5 A shows the results in the red region. The addition of the alcohol did increase the optical density and the optical density difference, but the shape of the curve remained the same. The difference in optical density between 0.8 and 0.9 mole fraction NCS^- was the same value in both water and water-alcohol systems. In the blue region the optical density due to the cobalt(II) ion and Co(NCS)^+ ion was very low in water solutions and an increase due to the addition of alcohol would be small. Hence in water-alcohol systems of cobalt-thiocyanate

FIGURE 4

COMPLEXATION SHOWN USING
JOB'S METHOD
(WATER SOLUTIONS)



1. $\text{Co}_{(\text{II})}$, NCS^- AT 520 $\text{M}\mu$
 2. SAME AT 500 $\text{M}\mu$
 3. SAME AT 480 $\text{M}\mu$
 4. SAME AT 460 $\text{M}\mu$
 5. SAME AT 560 $\text{M}\mu$
- (0.200 M SOLUTIONS)

TABLE IV

Data for Job's Method
(Water Solutions)

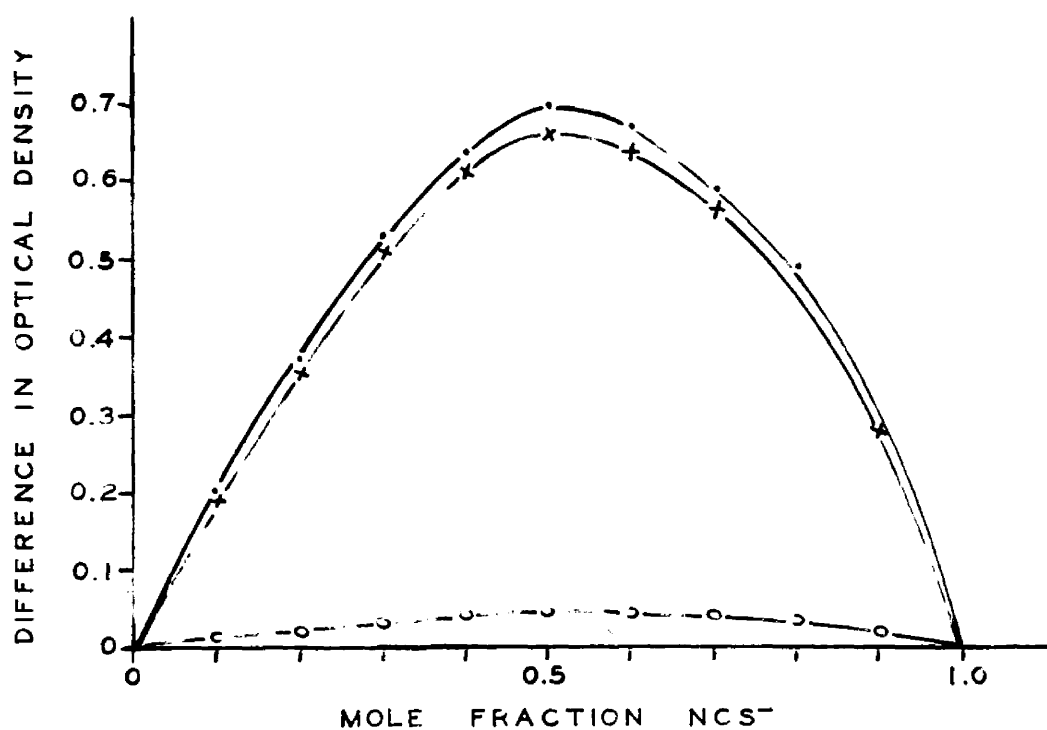
B. Slit Width at 0.02 mm.

Solution	Mole Fraction NCS ⁻	D (Optical Density) at Wave Lengths in mμ			D' Co(II) Diluted at Wave Lengths in mμ			D - D' at Wave Lengths in mμ		
		500	510	620	500	510	620	500	510	620
1	0.10	0.93	0.98	0.059	0.74	0.78	0.053	0.19	0.20	0.006
2	0.20	1.01	1.07	0.057	0.66	0.70	0.047	0.35	0.37	0.010
3	0.30	1.08	1.14	0.057	0.57	0.61	0.042	0.51	0.53	0.015
4	0.40	1.10	1.16	0.056	0.49	0.52	0.036	0.61	0.64	0.020
5	0.45	1.07	1.13	0.052	0.45	0.47	0.033	0.62	0.66	0.019
6	0.50	1.07	1.13	0.051	0.41	0.43	0.030	0.66	0.70	0.021
7	0.55	1.02	1.07	0.049	0.37	0.39	0.027	0.65	0.68	0.022
8	0.60	0.97	1.02	0.045	0.33	0.35	0.024	0.64	0.67	0.021
9	0.70	0.81	0.86	0.037	0.25	0.26	0.018	0.56	0.60	0.019
10	0.80	0.63	0.67	0.028	0.16	0.18	0.012	0.47	0.49	0.016
11	0.90	0.33	0.35	0.015	0.08	0.08	0.007	0.25	0.27	0.008
12	0.00	0.82	0.87	0.058	-	-	-	-	-	-

FIGURE 4

COMPLEXATION SHOWN USING
JOB'S METHOD
(WATER SOLUTIONS)

B. SLIT WIDTH AT 0.02 MM.



1. $\text{Co}(\text{II})$, NCS^- AT 510 $\text{M}\mu$
 2. SAME AT 500 $\text{M}\mu$
 3. SAME AT 620 $\text{M}\mu$
- (0.443 M SOLUTIONS)

TABLE V

Data for Job's Method
(Water-Alcohol Solutions)

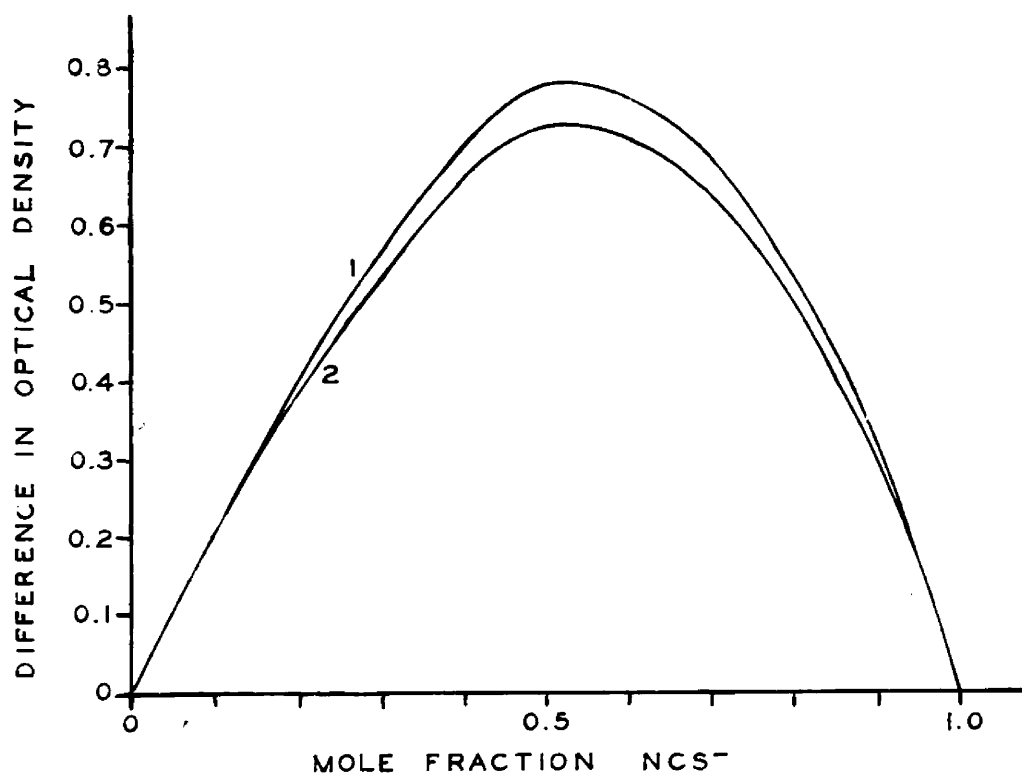
A. Slit Width at 0.02 mm.

Solution	Mole Fraction NCS ⁻	D (Optical Density)		D' Co(II) Diluted		D - D'	
		500 mμ	510 mμ	500 mμ	510 mμ	500 mμ	510 mμ
1	0.10	0.98	1.03	0.77	0.82	0.21	0.21
2	0.20	1.07	1.13	0.68	0.73	0.39	0.40
3	0.30	1.14	1.22	0.60	0.65	0.54	0.57
4	0.40	1.18	1.25	0.51	0.55	0.67	0.70
5	0.50	1.15	1.24	0.42	0.46	0.73	0.78
6	0.60	1.07	1.13	0.35	0.37	0.72	0.76
7	0.70	0.89	0.95	0.25	0.27	0.64	0.68
8	0.80	0.66	0.71	0.16	0.18	0.50	0.53
9	0.85	0.53	0.57	0.12	0.13	0.41	0.44
10	0.90	0.36	0.39	0.08	0.09	0.28	0.30
11	0.00	0.86	0.91	-	-	-	-

FIGURE 5

COMPLEXATION SHOWN USING
JOB'S METHOD
(WATER-ALCOHOL SOLUTIONS)

A. SLIT WIDTH AT 0.02 MM.



A.

1. Co(II) , NCS^- AT 510 $\text{M}\mu$
AND 520 $\text{M}\mu$
2. SAME AT 500 $\text{M}\mu$
(0.443 M SOLUTIONS)

the optical density in the blue region was so predominately due to the new species of cobalt thiocyanate ion formed that the optical density caused by cobalt and $\text{Co}(\text{NCS})^{\dagger}$ ions could be disregarded. The shape of the curve obtained by Job's method remained essentially the same and valid deductions could be made from it. At both slit widths (Figure 5 B and C) and several wave lengths the maximum optical density occurred in the region 0.85 to 0.86 mole fraction NCS^- . This corresponded to a complex of the composition $\text{Co}(\text{NCS})_6^{\equiv}$.

Although every position in the coordination sphere is occupied, a series of solutions were investigated to determine if the alcohol coordinated. Both 1 to 1 and 1 to 6 cobalt-thiocyanate ratios were used. Ethyl alcohol at more than forty times the molar concentration of the $\text{Co}(\text{NCS})^{\dagger}$ and of $\text{Co}(\text{NCS})_6^{\equiv}$ was required before the first sign of the characteristic blue hue was discerned thus indicating that there was no alcohol coordinating in the complex.

The formation of the $\text{Co}(\text{NCS})_6^{\equiv}$ ion was also shown by means of a spectrophotometric titration (39). A number of solutions were prepared all containing the same concentration of cobalt. Different amounts of NCS^- were added ranging from 0 to 15 times the amount of cobalt present. Figure 6 A gives the results in water solution and Figure 6 B those in 50% ethyl alcohol solution. Coordination combinations are indicated by a break in the slope of the curve, Optical Density versus the ratio of NCS^- to $\text{Co}(\text{II})$. The optical densities of the water solutions were measured at 510 mu. A break in slope was observed at a ratio of $\text{Co}(\text{II})$ to NCS^- of 1 to 1. At a ratio of 1 to 6 a slight break was also observed. The concentration of cobalt ion, 0.00885 M, was much too low for optical density measurements at 620 mu. Alcoholic solutions had a pronounced break at cobalt to thiocyanate ratios of 1 to 6 measured at a

TABLE V

Data for Job's Method
(Water-Alcohol Solutions)

B. Slit Width at 0.04 mm.

Solution	Mole Fraction NCS ⁻	D (Optical Density)	
		600 mμ	620 mμ
1	0.10	0.074	0.062
2	0.20	0.077	0.062
3	0.30	0.087	0.070
4	0.40	0.108	0.090
5	0.50	0.142	0.128
6	0.60	0.207	0.205
7	0.70	0.308	0.330
8	0.80	0.409	0.458
9	0.82	0.430	0.488
10	0.84	0.432	0.493
11	0.85	0.445	0.501
12	0.86	0.437	0.501
13	0.88	0.422	0.485
14	0.90	0.385	0.444
15	0.95	0.258	0.302
16	0.00	0.068	0.059

TABLE V

Data for Job's Method
(Water-Alcohol Solutions)

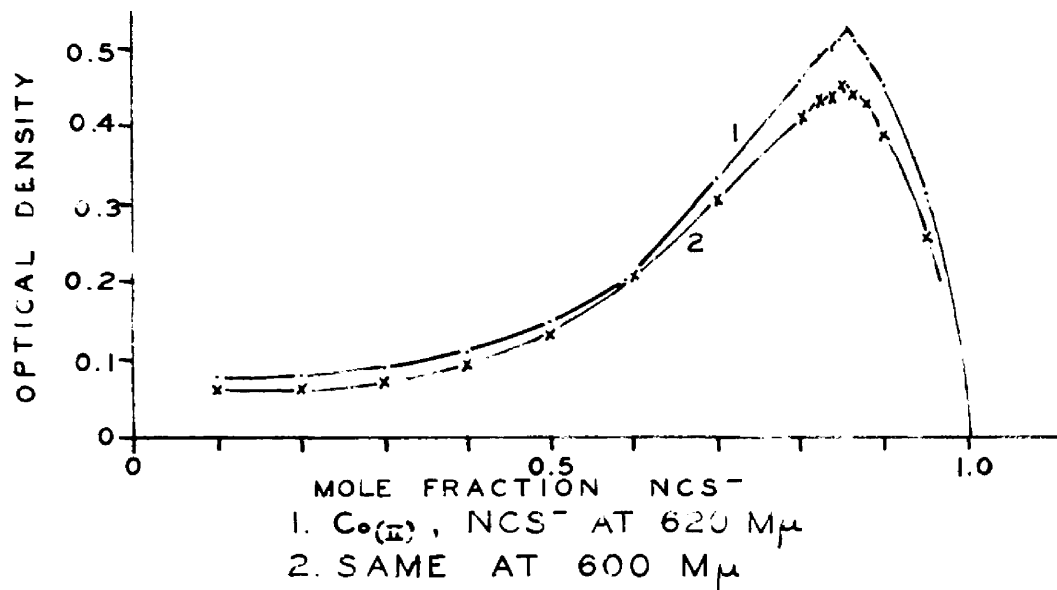
C. Slit Width at 0.15 mm.

Solution	Mole Fraction NCS ⁻	D (Optical Density)		
		590 mμ	600 mμ	620 mμ
1	0.50	0.162	0.150	0.152
2	0.60	0.214	0.219	0.238
3	0.70	0.280	0.313	0.356
4	0.80	0.330	0.385	0.452
5	0.82	0.337	0.397	0.468
6	0.84	0.343	0.409	0.481
7	0.86	0.340	0.403	0.474
8	0.88	0.316	0.384	0.455
9	0.90	0.293	0.356	0.425
10	0.92	0.263	0.317	0.382
11	0.94	0.219	0.266	0.322
12	0.96	0.173	0.208	0.250
13	0.98	0.064	0.117	0.144

FIGURE 5

COMPLEXATION SHOWN USING
JOB'S METHOD
(WATER-ALCOHOL SOLUTIONS)

B. SLIT WIDTH AT 0.04 MM.



C. SLIT WIDTH AT 0.15 MM.

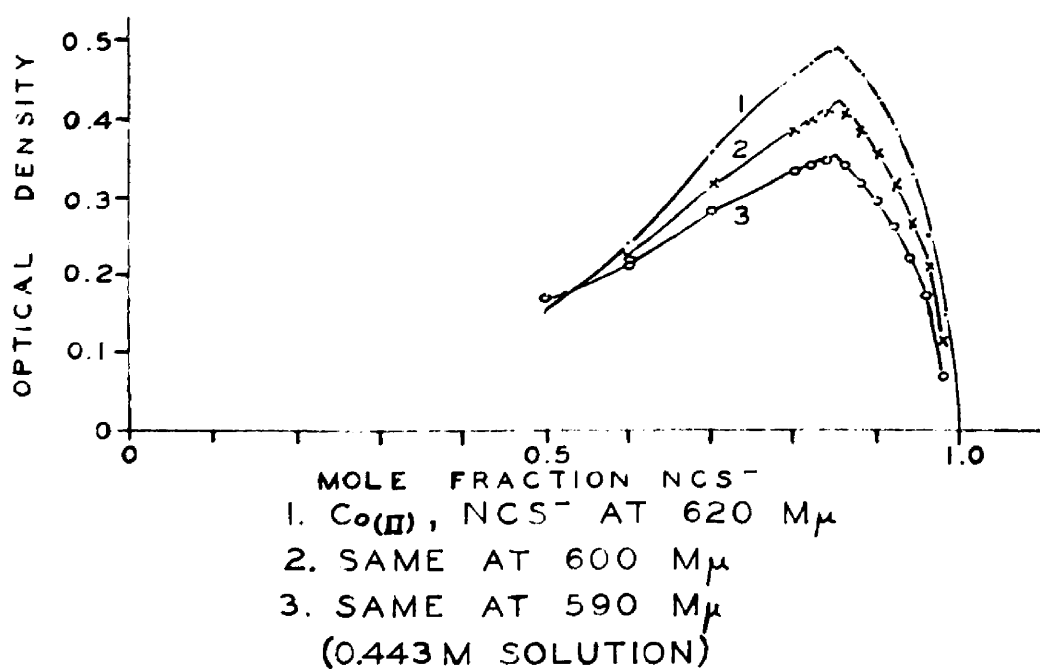


TABLE VI

Data for Spectrophotometric Titration

A. Water Solutions

Solution	Ratio of $\frac{\text{HCO}_3^-}{\text{Co(II)}}$	D (Optical Density) 510 mμ
1	0.000	0.043
2	0.515	0.054
3	2.58	0.090
4	3.87	0.103
5	5.15	0.116
6	7.72	0.132
7	10.3	0.144
8	12.9	0.151
9	15.5	0.163

FIGURE 6
SPECTROPHOTOMETRIC TITRATION

A. WATER SOLUTION 0.00885 M $\text{Co}(\text{II})$

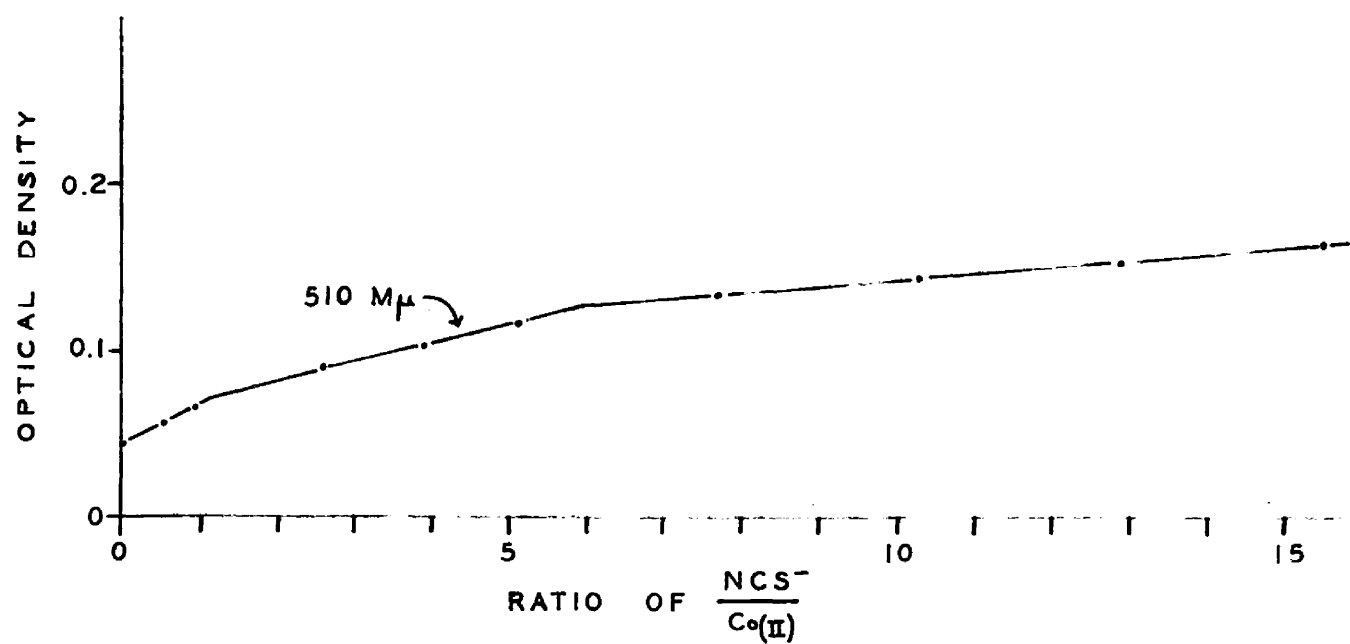


TABLE VI

Data for Spectrophotometric Titration

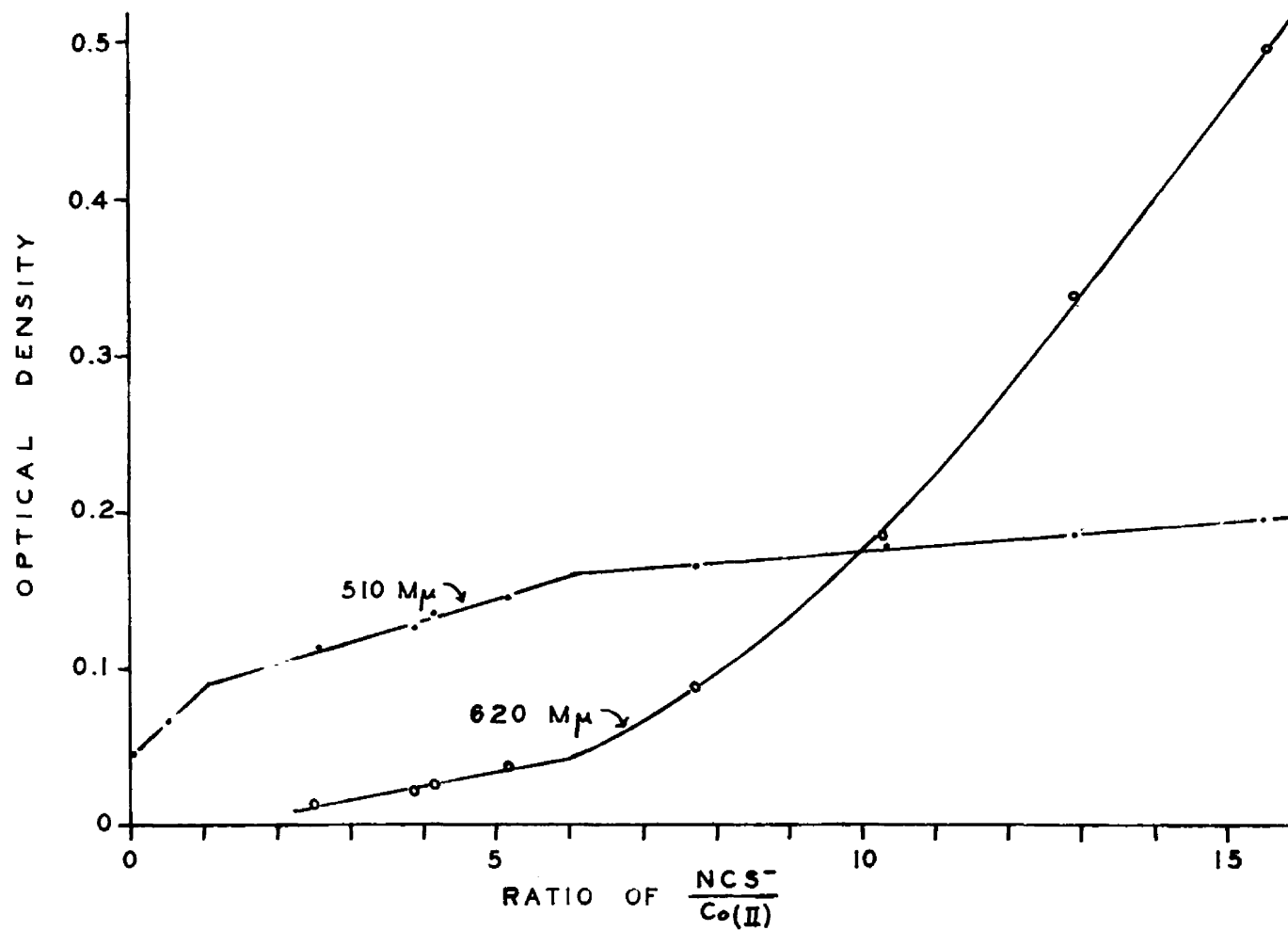
B. Water-Alcohol Solutions

Solution	Ratio of $\frac{\text{NCS}^-}{\text{Co(II)}}$	D (Optical Density)	
		510 mμ	620 mμ
1	0.000	0.045	-
2	0.515	0.065	-
3	2.58	0.113	0.014
4	3.87	0.127	0.020
5	4.12	0.134	0.024
6	5.15	0.145	0.037
7	7.72	0.165	0.089
8	10.3	0.179	0.183
9	12.9	0.185	0.339
10	15.5	0.196	0.495

FIGURE 6

SPECTROPHOTOMETRIC TITRATION

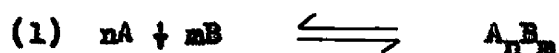
B. WATER-ALCOHOL SOLUTIONS 0.00885 M $\text{Co}(\text{II})$



wave length of 620 mu. The optical density was too low for readings in the 1 to 1 ratio range. At the wave length of 510 mu the 1 to 1 and 1 to 6 ratios of Co(II) to NCS⁻ were shown as in the water solution.

In an attempt to confirm further the results already obtained in this study, the limiting logarithmic method (2) was applied.

Consider the following chemical reaction:



where n moles of A react with m moles of B to form the product A_nB_m .

The equilibrium constant for this reaction may be expressed by

$$(2) \quad K = \frac{[A_nB_m]}{[A]^n [B]^m}$$

or

$$(3) \quad [A]^n [B]^m K = [A_nB_m]$$

and taking the log of both sides the following expression was derived:

$$(4) \quad n \log [A] + m \log [B] + \log K = \log [A_nB_m]$$

If A_nB_m exhibits a color, the amount of A_nB_m formed is related to the optical density of the solution. In this method, if the concentration of A is held constant the change in optical density is observed when the concentration of B is varied. With $[A]$ held constant the equation may be written

$$(5) \quad \log D = m \log [B] + k$$

with $k = \log EK [A]^n$ where E is the extinction coefficient and D is the optical density. Equation (5) is of the straight line form with slope m when log D is plotted versus log $[B]$. In the equation developed the slope m gives the amount of B complexing when log D is plotted against log $[B]$. Also, by holding the concentration of B constant and varying

the concentration of A, the number of A particles, n, coordinated with B can be determined.

Table VII summarizes the data obtained at 620 mμ shown graphically in Figure 7. The slope of the Co(II) curve was 0.428 and that of the NCS⁻ curve was 2.57 giving a slope ratio of 1 to 6.

This investigator attaches no significance to the ratio of slopes because the absolute values of the slopes should have been 1 and 6. The limiting logarithmic method assumes that the amount of A_nB_m formed is negligible compared to the amounts of A and B; and further, that the concentrations of A and B at equilibrium are essentially the same as before the reaction occurred. Since Job's method of continuous variation showed $Co(NCS)^{\dagger}$ to be present in blue colored solutions the concentrations of A and B at equilibrium are not the same as the initial concentrations even if only a slight amount of A_nB_m were formed. These observations combined with the fact that an appreciable amount of A_nB_m could have been formed (there is no proof pro or con) suggest that the slope ratio of 1 to 6 is merely circumstance.

At extreme dilutions of cobalt(II) and concentrated solutions of thiocyanate no straight line could be obtained using this method.

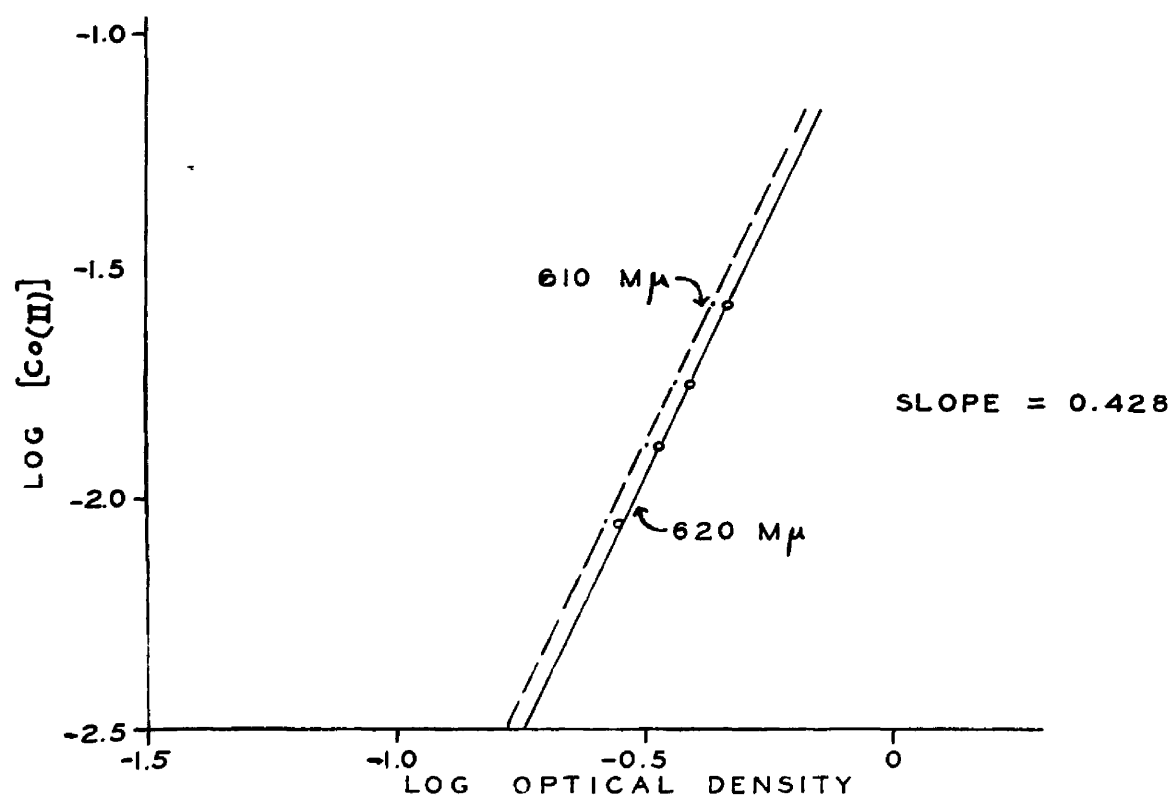
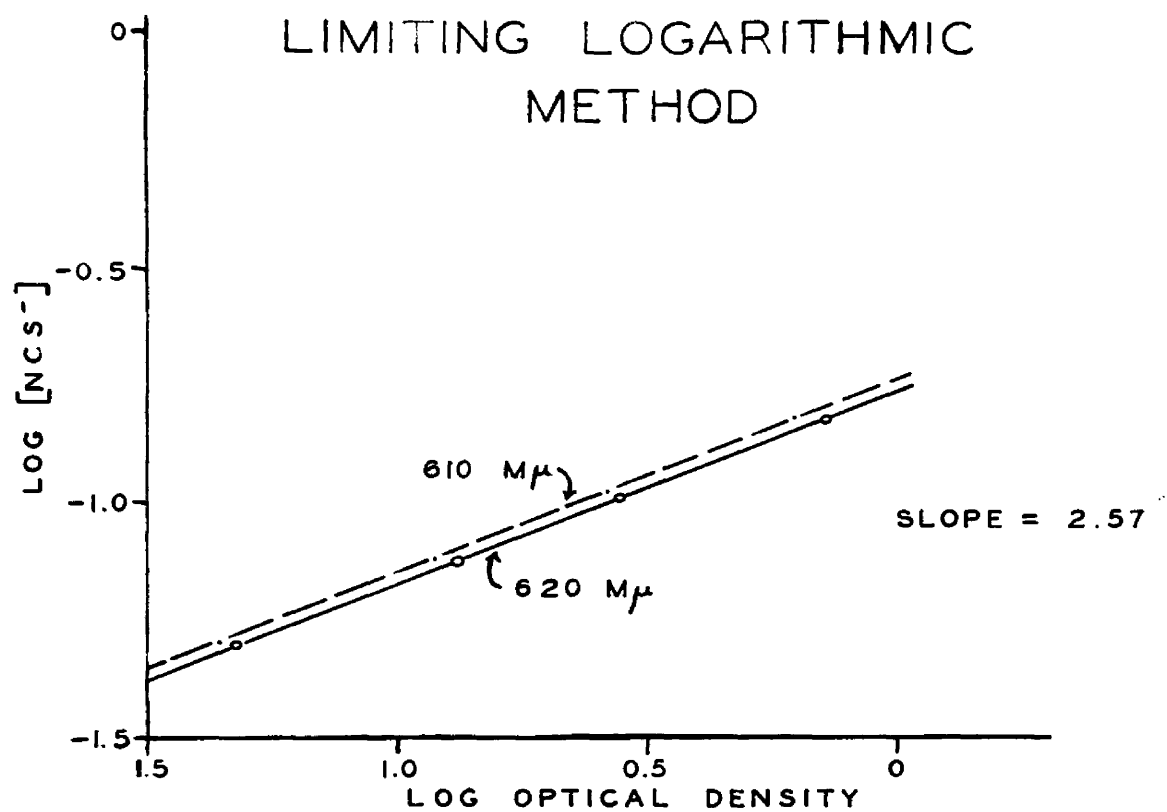
TABLE VII

Data for Limiting Logarithmic Method

Solution	Concentration Co(II)	Concentration NCS ⁻	Log C	D (Optical Density)		Log D	
				610 mμ	620 mμ	610 mμ	620 mμ
1	0.00885M	0.0507M	-1.295	0.045	0.047	-1.346	-1.328
2	0.00885M	0.0760M	-1.119	0.123	0.130	-0.910	-0.886
3	0.00885M	0.101M	-0.994	0.262	0.274	-0.572	-0.562
4	0.00885M	0.152M	-0.818	0.684	0.695	-0.165	-0.158
5	0.00885M	0.101M	-2.053	0.262	0.274	-0.572	-0.562
6	0.0133M	0.101M	-1.876	0.323	0.337	-0.491	-0.472
7	0.0177M	0.101M	-1.752	0.373	0.389	-0.428	-0.410
8	0.0266M	0.101M	-1.575	0.440	0.457	-0.356	-0.340

50% Ethyl Alcohol Solutions

FIGURE 7

LIMITING LOGARITHMIC
METHOD

DISCUSSION OF RESULTS AND CONCLUSIONS

A change of color in a system may indicate a change in ionic structure. Cobalt(II)-alcohol-water systems are involved in such a change when either thiocyanate or thiosulfate ions are added. Since their ionic weights are quite different if either of these ions were added to the cobalt ion as addenda, the ionic weights of the resulting complex would be different. Chloride ions in the concentrations used do not produce any color change.

Polarographic studies have been made on various cobalt-thiocyanate systems and the following statements can be made: in water-alcohol solutions containing cobalt(II) ions and chloride or thiosulfate or thiocyanate ions, the ions diffusing into the mercury drop and being reduced were of the same weight. Such a result indicated that the cobalt complex formed in causing a change from a pink to blue color was unstable under the conditions of these experiments and was disrupted in each case into a cobalt ion, perhaps of the structure $\text{Co}(\text{H}_2\text{O})_6^{++}$, before reduction occurred. This was reflected by the diffusion current, i_d , since it was the same for similar concentrations of cobalt(II) ions, of the supporting electrolyte and of the alcohol.

Spectrophotometric studies showed the formation of a pink complex in water solutions with a ratio of cobalt to thiocyanate of 1 to 1. Job's method and the method of spectrophotometric titration both gave this result. By the latter method the complex $\text{Co}(\text{NCS})_6^{2-}$ in water solution was also indicated. Both methods proved the blue color resulted from the formation of $\text{Co}(\text{NCS})_6^{2-}$ ions produced in

alcoholic solutions.

Application of the limiting logarithmic technique to alcoholic solutions gave a slope ratio of cobalt to thiocyanate of 1 to 6 at 680 m μ . However, the restrictions required of this method were not met by the system and the slope ratio obtained probably has no real significance in establishing the combination in the complex.

The same spectral characteristics are shown by absorbancy curves of blue cobalt solutions regardless of the anion or alcohol used in the development of color. This indicates that the change in color from pink to blue is associated with configurations within the cobalt atom itself.

This investigator recommends magnetic susceptibility studies for future investigations. Perhaps the type of electron change within the cobalt atom could be shown and the relative amounts of the blue and red forms of cobalt(II) could be determined. Raman spectra studies might also prove advantageous in future research on this problem.



SUMMARY

1. The Vogel reaction has been investigated both polarographically and spectrophotometrically.
2. No change in ionic weight in the transition from the pink to blue colored solution was indicated by polarographic studies when using either the absolute or comparative methods of ionic weight determination.
3. In the course of the polarographic investigations the selenocyanate ion was found to give the Vogel blue and these organic solvents: formic acid, n-butyl alcohol, isopropyl alcohol, n-propyl alcohol, diethylene glycol, tert-amyl alcohol, methyl alcohol and tert-butyl alcohol hitherto unreported, were found to develop the blue color.
4. The structure of the ion responsible for the deepening of color at a wave length of 620 mμ in alcoholic solutions could not be deduced by the curve variation method. A deepening of color was produced when either the ratio of thiocyanate to cobalt(II) or alcohol to water was increased.
5. The method of continuous variation showed the complex $\text{Co}(\text{NCS})^+$ present in pink aqueous solutions of cobalt and thiocyanate ions when measurements were made at wave lengths of 510 and 620 millimicrons. In blue alcoholic solutions at the wave length of 620 millimicrons the complex $\text{Co}(\text{NCS})_6^{2-}$ was shown to be present.
6. The method of spectrophotometric titration at a wave length of 510 millimicrons showed the presence of $\text{Co}(\text{NCS})^+$ and $\text{Co}(\text{NCS})_6^{2-}$ in water

solutions and in alcoholic solutions; at 620 millimicrons the titration showed the formation of the complex $\text{Co}(\text{NCS})_6^{\frac{3-}{2}}$ in alcoholic solutions of cobalt(II) and thiocyanate ions.

7. When the limiting logarithmic method was applied to alcoholic solutions at a wave length of 620 mu the data did not give results of immediate significance because of uncertainties concerning the condition of the system at equilibrium.

8. Since various addenda and alcohols gave complexes having the same spectral characteristics the blue color was proposed to be associated with configurations within the cobalt atom itself.

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VITA

Charles Gosse de Vries was born in Wheeling, West Virginia, on June 27, 1919, the second son of Gosse Bote and Ruth Winchester de Vries. Elementary education was received in the public schools of West Virginia. He graduated from Ceredo-Kenova High School, Kenova, West Virginia, in May, 1937.

The following September, he entered Marshall College and after two years of study, transferred to West Virginia University. Upon graduation with a Bachelor of Arts Degree in June, 1941, he accepted a position with the American Viscose Corporation.

He terminated his association with this company on February 13, 1943 upon entering the Army of the United States. After serving in the Medical Corps and Ordnance Department, he was honorably discharged on February 10, 1946.

In the same month, he entered Louisiana State University Graduate School and served as a graduate assistant during the fall term of 1946-47. From February, 1947 to June, 1949 he served as a research assistant.

On August 20, 1947 he was married to Laura Brown Lynch of Baltimore, Maryland.

In June, 1948 he received the Master of Science Degree from Louisiana State University and he is now a candidate for the degree of Doctor of Philosophy in Chemistry.

EXAMINATION AND THESIS REPORT

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Major Field: **Chemistry**

Title of Thesis: **A Study of the Vogel Reaction for the Determination of Cobalt**

Approved:

Philip W. West
Major Professor and Chairman

W. S. Deringer
Dean of the Graduate School

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Date of Examination:

May 11, 1949